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TITLE OF INVENTION: CLINKER HYDRAULIC BINDER, USE AND METHOD FOR MAKING SAME

APPLICANT(S) FOR DO/EO/US: Jean-Pierre FALASCHI, Herve FRYDA, Jean-Pierre LETOURNEUX, Christopher PARR, Bruno TOUZO, Michel VIALLE

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
 2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
 3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
 4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau. (see attached copy of PCT/IB/308)
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
 6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
 7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
 8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
 10. ☐ A translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Item 11. to 16. below concern document(s) or information included:
11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
 13. ☒ A **FIRST** preliminary amendment.
 14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
 15. ☐ A substitute specification.
 16. ☐ A change of power of attorney and/or address letter.
 16. ☒ Other items or information:

International Search Report
 PCT/IB/308
 PCT/IPEA/409
 Abstract of the Disclosure on a Separate Sheet
 Application Data Sheet

U.S. APPLICATION NO. (if known, see 37 CFR 1.53)

09/890144

INTERNATIONAL APPLICATION NO.
PCT/FR00/00167ATTORNEY'S DOCKET NO.
165K US 380617. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):**

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$ 1,000.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$ 860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$ 710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$ 690.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$ 100.00

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Surcharge of \$130.00 for furnishing the oath or declaration later than 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total Claims	20 - 20 =	0	X \$18.00	\$
Independent claims	1 - 3 =	0	X \$80.00	\$
MULTIPLE DEPENDENT CLAIMS(S) (if applicable)			+ \$270.00	\$
TOTAL OF ABOVE CALCULATIONS =				\$ 990.00
Reduction of 1/2 for filing by small entity, if applicable. Applicant claims Small Entity Status under 37 CFR 1.27.				+
SUBTOTAL =				\$ 990.00
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TOTAL NATIONAL FEE =				\$ 990.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$
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July 26, 2001

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PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Jean-Pierre FALASCHI et al.

Serial No. (unknown)

Filed herewith

CLINKER HYDRAULIC BINDER,
USE AND METHOD FOR MAKING SAME

PRELIMINARY AMENDMENT

Commissioner for Patents

Washington, D.C. 20231

Sir:

Prior to calculation of the filing fee, please
amend the above-identified application as follows:

IN THE CLAIMS:

Amend claim 5 as follows:

--5. (Amended) Binder according to claim 1,
characterized in that it is quasi-free from free residual
MgO, at least as it can be observed on X-ray diffraction
spectrum for the binder.

Amend claim 6 as follows:

--6. (Amended) Binder according to claim 1,
characterized in that it has the following chemical composi-
tion by dry weight of the binder :

- lime CaO : 4 to 12%

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- magnesia MgO : 19 to 23%
- alumina Al_2O_3 : 69 to 74%.

Amend claim 8 as follows:

--8. (Amended) Binder according to claim 1, characterized in that it comprises a SiO_2 content of less than 0.5% of the binder by dry weight.

Amend claim 9 as follows:

--9. (Amended) Binder according to claim 1, characterized in that it has a Blaine area surface at least equal to $3000 \text{ cm}^2/\text{g}$.

Amend claim 10 as follows:

--10. (Amended) Use of a binder according to claim 1 for producing a refractory concrete.

Amend claim 13 as follows:

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--13. (Amended) Use of a binder according to claim 1, characterized in that it is used in the manufacture of steel ladles (1), preferably for wear linings (5) of such steel ladles (1).

Amend claim 14 as follows:

--14. (Amended) Process for producing a binder according to claim 1, characterized in that the binder is made through frittering by burning of a blend of raw materials comprising dolomite, alumina and magnesia.

Amend claim 16 as follows:

--16. (Amended) Process according to claim 14, characterized in that alumina is metallurgical.

Amend claim 17 as follows:

--17. (Amended) Process according to claim 14, characterized in that magnesia is reactive, preferably caustic, and has advantageously a grain size 100% lower than 100 μm , preferably lower than 40 μm .

Amend claim 18 as follows:

--18. (Amended) Process according to claim 14, characterized in that, before burning, the raw materials are milled up to a grain size corresponding to a 2% maximum rejection in a sieve of 65 μm .

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Amend claim 19 as follows:

--19. (Amended) Process according to claim 14, characterized in that burning is carried out at a temperature comprised between 1400°C and 1600°C.

Amend claim 20 as follows:

--20. (Amended) Process according to claim 14, characterized in that the degree of progression of the burning is evaluated by measuring the free magnesia content by dry weight of the mixture.--

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R E M A R K S

The above changes in the claims merely place this national phase application in the same condition as it was during the international phase, with the multiple dependencies being removed.

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE".

Respectfully submitted,

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July 26, 2001

VERSION WITH MARKINGS TO SHOW CHANGES MADE

The claims have been amended as follows:

5. (Amended) Binder according to ~~any one of claims 1 to 4~~claim 1, characterized in that it is quasi-free from free residual MgO, at least as it can be observed on X-ray diffraction spectrum for the binder.

6. (Amended) Binder according to ~~any one of claims 1 to 5~~claim 1, characterized in that it has the following chemical composition by dry weight of the binder :

- lime CaO : 4 to 12%
- magnesia MgO : 19 to 23%
- alumina Al₂O₃ : 69 to 74%.

8. (Amended) Binder according to ~~any one of claims 1 to 7~~claim 1, characterized in that it comprises a SiO₂ content of less than 0.5% of the binder by dry weight.

9. (Amended) Binder according to ~~any one of claims 1 to 8~~claim 1, characterized in that it has a Blaine area surface at least equal to 3000 cm²/g.

10. (Amended) Use of a binder according to ~~any one of claims 1 to 9~~claim 1 for producing a refractory concrete.

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13. (Amended) Use of a binder according to ~~any one of claims 10 to~~ claim 12, characterized in that it is used in the manufacture of steel ladles (1), preferably for wear linings (5) of such steel ladles (1). 14. (Amended) Process for producing a binder according to ~~any one of claims 1 to 9~~ claim 1, characterized in that the binder is made through frittering by burning of a blend of raw materials comprising dolomite, alumina and magnesia.

16. (Amended) Process according to ~~any one of claims 14 or 15~~ claim 14, characterized in that alumina is metallurgical.

17. (Amended) Process according to ~~any one of claims 14 to 16~~ claim 14, characterized in that magnesia is reactive, preferably caustic, and has advantageously a grain size 100% lower than 100 µm, preferably lower than 40 µm.

18. (Amended) Process according to ~~any one of claims 14 to 17~~ claim 14, characterized in that, before burning, the raw materials are milled up to a grain size corresponding to a 2% maximum rejection in a sieve of 65 µm.

19. (Amended) Process according to ~~any one of claims 14 to 18~~ claim 14, characterized in that burning is carried out at a temperature comprised between 1400°C and 1600°C.

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20. (Amended) Process according to ~~any one of~~
~~claims 14 to 19~~claim 14, characterized in that the degree
of progression of the burning is evaluated by measuring the
free magnesia content by dry weight of the mixture.

5/PR18

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JC18 Rec'd PCT/PTO 26 JUL 2001

CLINKER HYDRAULIC BINDER, USE AND METHOD
FOR MAKING SAME

The present invention relates to a clinker-type hydraulic binder obtained
5 by burning comprising a magnesia spinel mineralogical phase and at least one
calcium aluminate mineralogical phase, with a lime content of less than 15% of
the binder by dry weight. It also relates to the use and a method of making such
a binder.

Ladle steel metallurgy has developed these last years up to become a
10 key point in the steel-manufacturing process. A ladle is a real chemical reactor
with internal temperatures adapted to reach 1700°C and being able to contain
up to 300 tonnes of melted material. Conventionally used refractory concretes
(first shaped, and then more and more monolithic) in steel ladles are not
satisfactory any more and the performances thereof in such a field have to be
15 improved.

In particular, the steel ladles contain wear linings in contact with steel
and slag and more particularly exposed to slag infiltration and corrosion. Such
wear linings should be able to best resist such aggressions.

More particularly there is an interest for monolithic concretes with low
20 lime content (lower than 2.5% by dry weight in concrete) so-called LCC
concretes (Low Cement Concrete), and with very low lime content (lower than
1% by dry weight in concrete) so-called ULCC concretes (Ultra Low Cement
Concrete). The low lime content of such concretes is advantageous for
obtaining a high refractoriness required for applications with steel ladles.

The Applicant has described in publication UNITECR'97, vol. III,
25 pp. 1347-1354 (1997) of N. Blunt, C. Revais and M. Vialle entitled "Additives in
calcium aluminate cement containing castables", a study over castable
monolithic refractory concrete types based on a blend of aluminous cement and
magnesian spinel, particularly with a low lime content. The magnesian spinel
30 and calcium aluminates contained in the aluminous cement have therein
functions of refractory component et hydraulic component.

The concretes being described in such a publication bring out difficulties
to reach a satisfactory rheology and an easy implementation.

Other solutions have been proposed to make refractory concretes
35 through a clinker based on magnesian spinel and calcium aluminates.

Thus, Patent FR-1,575,633 discloses an aluminous refractory cement produced from a blend of 30 to 50% dolomite and 50 to 70% calcined alumina by burning up to clinkerization or melting.

FR-2,043,678 is an addition certificate application attached to FR-1,575,633, which described an aluminous refractory cement based on magnesian spinel and calcium aluminates obtained from a blend of dolomite and calcined bauxite or calcined alumina, lime and magnesia, through burning up to clinkerization or melting.

Japanese Patent Application JP-8-198649 is per se relative to a composition of refractory cement or concrete based on a calcium aluminate material prepared from lime, alumina and magnesia, through melting and/or calcination.

The compositions of the three above-mentioned last documents have the inconvenient that they are not sufficiently well adapted for refractory applications in steel ladles, particularly for producing LCC or ULCC concretes able to resist slag infiltration in steel ladles and resulting corrosion.

The invention relates to a clinker-type hydraulic binder obtained by burning particularly adapted for producing steel ladles and having a very high resistance to slag infiltration and corrosion compared particularly to the known binders.

The binder according to the invention allows to produce refractory monolithic concretes LCC or ULCC based on magnesian spinel, making possible an implementation with very satisfactory reactivity (setting time) and rheology (fluidity, castability).

The invention also relates to the use of such a binder for making a refractory concrete.

It has also as an object a process for making such a binder, making possible an easy implementation from currently available raw materials and advantageously at a low burning temperature (lower than 1800°C).

Other advantages associated with the binder according to the invention, besides the refractoriness and the resistance to slag infiltration and corrosion, include the following ones :

- cancellation of the $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (so indicated C_{12}A_7), except possibly in a strongly underburnt clinker and only on a temporary basis, such phase being able to bring about stiffening difficulties in concrete formulations;

- binder microstructure being advantageous for the milling thereof so as to reach high granular fineness, so improving the corrosion resistance;
- very low content in free residual magnesia, i.e. non combined in magnesian spinel, so as to be able to prevent the generation of cracks due to free magnesia in brucite during the implementation step for the refractory concrete produced from the binder.

Thus, an object of the invention is a clinker-type hydraulic binder obtained through burning comprising :

- a magnesian spinel mineralogical phase, and
- at least a calcium aluminate mineralogical phase with a lime content of less than 15% of the binder by dry weight.

According to the invention, the magnesian spinel comprises between 68% and 81% of the binder by dry weight.

Surprisingly such high proportions of the magnesian spinel allow to obtain the above-mentioned advantages, in particular good corrosion resistance properties.

By contrast, the known clinker-type binders comprising magnesian spinel and calcium aluminates and with a lime content of less than 15% have substantially lower magnesian spinel contents. In particular, FR-1,575,633 and FR-2,043, 678 disclose proportions comprised between 25 and 45% magnesian spinel.

JP-8-198649 relates as per se to a binder with a lime content comprised between 15% and 30%, thus inappropriate for making LCC or ULCC concretes.

The term "clinker-type binder" means not only the proper clinker, thus the product before milling, but also the clinker being milled.

Such a clinker may be produced either at high temperature (higher than 1800°C) by melting, for example in an electric oven, or advantageously through calcination (sintering) at low temperature (lower than 1800°C).

Preferably, the binder is used for making concrete to which it gives magnesian spinel fine particles. The concrete formulation is then advantageously supplemented by fine reactive aluminas and by large magnesia spinel, as well as other granulates.

The high proportion of magnesian spinel in the binder allows to supply the total fine spinel of the concrete while preventing the problems encountered with a direct mixture of aluminous cement and magnesian spinel, as in

UNITECR'97 above-mentioned. Moreover, the so-made concrete may have a low or very low lime content.

Preferably, the calcium aluminates are all under crystallized form.

More precisely, it is advantageous that the calcium aluminates should
5 be essentially made of CA and CA₂, with CA being CaO and A being Al₂O₃.

Such a binder composition, with a pattern MA-CA-CA₂ (with M=MgO), leads to such a surprising and advantageously consequence that the presence of C₁₂A₇ is prevented, such a phase being adapted to lead to a stiffening cement.

10 Advantageously the calcium aluminates CA and CA₂ comprise between 19% and 32% of the binder by dry weight. More particularly it is strongly interesting the binder should comprise by dry weight of the binder :

- 71 ± 2% MA (magnesian spinel)
- 18 ± 2% CA, and
- 15 - 11 ± 2% CA₂.

Such a composition is in thermodynamic equilibrium in the CaO-MgO-Al₂O₃ system, so that C₁₂A₇ cannot be present in this combination, except possibly in a strongly underburnt clinker and on a temporary basis.

20 In an alternative embodiment, the calcium aluminates are present under an amorphous form, particularly under a vitreous form.

Preferably, the binder is quasi-free from free residual MgO at least as it can be observed on X-ray diffraction spectrum for the binder.

Practically the X-ray diffraction technique allows to insure that the free magnesia is present in a lower proportion than 0.5% of the binder by dry weight.

25 Thus, the magnesia present in the raw material is almost combined into spinel. During the keramization step of a refractory concrete from the binder, since the hydraulic concrete dehydration may lead to a high steam pressure inside the concrete, crack generations due to the hydration of the magnesia into brucite are thus prevented.

30 By reference to UNITECR'97, the so-obtained concrete may further possess a particularly advantageously microstructure, since it comprises an intergranular matrix (between granulates of big size) formed with much finer grains. Such a property is due to the fact that the magnesian spinel in the binder can be easily milled and makes possible to produce very fine grains.

35 Preferably, the binder has the following chemical composition by dry weight of the binder :

- lime CaO : 4 to 12%
- magnesia MgO : 19 to 23%
- alumina Al₂O₃ : 69 to 74%.

More specifically, the binder has advantageously the following
 5 chemical composition, by dry weight of the binder :

- lime CaO : 8,4%
- magnesia MgO : 20,4%
- alumina Al₂O₃ : 71,2%.

The binder comprises advantageously a SiO₂ content of less than 0.5%
 10 of the binder by dry weight.

Preferably, the binder has a Blaine area surface at least equal to
 3000 cm²/g and advantageously higher than 4000 cm²/g.

This entity is measured according to the NF EN 196-6 standard. The
 binder comprises such characteristic after milling the clinker, the limit value
 15 indicated giving a preferred level of fineness of the grains which may be
 obtained with the binder according to the invention.

Another object of the invention is the use of a binder according to the
 invention for producing a refractory concrete.

Preferably, the binder is complemented by magnesian spinel,
 20 preferentially of large size, so that the concrete contains between 20% and 30%
 magnesian spinel by dry weight of the concrete.

Such spinel proportion is particularly advantageously, since it allows to
 obtain good resistances both to corrosion and slag penetration.

More precisely the concrete is produced advantageously by mixing by
 25 dry weight of the binder :

- between 16 and 27% of the binder,
- between 2 and 13% of fine reactive alumina,
- between 0 and 19% of large spinel, and
- between 52 and 71% of alumina granulates.

30 In a particularly advantageous embodiment :

- 18% of the binder,
- 11% of fine reactive alumina,
- 11% of large spinel, and
- 60% of alumina granulates.

35 These proportions allow to produce a dense concrete with a theoretical
 compactness comprised between 0.25 and 0.40 because grain size lines are

used that can suit to Andreassen mathematical model. The above-mentioned compositions authorize the proportion of 20% to 30% magnesian spinel.

In alternative embodiments, the reactive alumina being mixed with the binder is substituted by other materials.

5 The binder according to the invention is advantageously used in the manufacture of steel ladles, preferably for wear linings of such steel ladles.

The invention also relates to a process for producing a binder as defined above. According to the invention, the binder is made through frittering by burning of a blend of raw materials comprising dolomite, alumina and
10 magnesia.

This blend, a source of CaO, MgO and Al₂O₃, has the advantage to give a very good sintering behaviour which can be appreciated by the quantity of uncombined magnesia staying after clinkerization.

Advantageously the raw materials have the following characteristics
15 separately or in combination :

- dolomite is natural : such dolomite leads, upon the decomposition thereof during the clinkerization, to the formation of very reactive products and has also the advantage to be economical;
- alumina is metallurgical : such alumina has this advantage to be very
20 reactive;
- magnesia is reactive, preferably caustic, and has advantageously a grain size 100% lower than 100 µm, preferably lower than 40 µm : magnesia fine grain size is particularly interesting, since it favours a total combination of magnesia and consequently prevents residual magnesia
25 to be present.

In two particularly advantageous embodiments, the following patterns are respectively used, where dolomite, alumina and magnesia are indicated by their tradenames :

- Dolomite Samin – Alumina Sandy – Magnesia Briquette
- 30 - Dolomite Samin – Alumina Pechiney – Magnesia MagChem40.

Preferably, before burning, the raw materials are milled up to a grain size corresponding to a 2% maximum rejection in a sieve of 65 µm.

This co-milling of the raw materials allows to accelerate the chemical reactions in a solid phase.

35 Burning is advantageously carried out at a temperature comprised between 1400°C and 1600°C.

Such relatively low burning temperatures are advantageous in the industrial and economical fields.

Advantageously, the degree of progression for burning is evaluated by measuring the free magnesia content by dry weight of the blend, for example by R-ray diffraction.

Such a content is in fact representative of the clinkerization being made.

When the clinker-type binder has been obtained, it is preferably milled. It is then advantageously used for making magnesian spinel based concrete.

The present invention will be illustrated and better comprised through particular embodiments, but without limiting the invention, referring to the annexed drawings wherein :

Fig. 1 shows in a longitudinal section a steel ladle manufactured for example with the binder according to the invention,

Fig. 2 shows an enlarged view of a part of the edges in the steel ladle of Fig. 1,

Fig. 3 shows the comparative grain size lines of the spinel of a binder according to the invention and of two common spinels,

Fig. 4 is a picture showing in a 200 x enlargement the microstructure after keramization of a known refractory concrete based on a direct blend of aluminous cement (commercially available under reference "S71") and magnesian spinel (as shown in Publication UNITECR' above-mentioned),

Fig. 5 is a picture showing with a 200 x enlargement the microstructure after keramization of a CMA refractory concrete obtained from a binder according to the invention,

Fig. 6 is a top view of a crucible used for corrosion tests,

Fig. 7 is a side view in section through the crucible of Fig. 6,

Fig. 8 represents a type profile through slag degradation of the crucible of Fig. 6 and 7,

Fig. 9 is a picture of a first crucible after a corrosion test at 1500°C and during 24 hrs, and

Fig. 10 is a picture of a second crucible after a corrosion test at 1500°C and during 24 hrs.

A clinker-type binder, comprising magnesian spinel representing between 68% and 81% by dry weight of the binder and calcium aluminates, is used for producing a refractory concrete used for manufacturing a steel ladle. Such a steel ladle 1 (Fig. 1) of a substantially frustro-conical shape comprises a

bottom 2, a side wall 3 and a cord 4 extending above the side wall 3. The steel ladle 1 is used for conveying melted metal, but may be provided with heating means to produce a heating 10 in the bottom 2. Such heating is for example carried out by induction. In an alternative embodiment, it is effected through dipping electrodes.

The edges 2, 3 and 4 of the steel ladle 1 comprise three successive linings 5, 6 and 7, from the inside to the outside of the ladle (Fig. 2), respectively a wear lining 5, an insulating lining 6 and a security lining 7.

Each of the three zones comprising the bottom 2, the side wall 3 and the cord 4 is formed from a distinct refractory concrete adapted for the given zone. The wear lining 5 of the side wall and the bottom is made of concrete produced from the above-defined binder.

In operation, the steel ladle 1 is used by increasing temperature of melted steel 11 up to high values (can reach 1700°C). Steel 11 in the steel ladle 1 is contained in a space limited by the bottom 2 and the side wall 3. It forms then above the steel 11 a slag 12 which is limited laterally by the cord 4.

Particular exemplary embodiments of the clinker-type binder are further detailed below.

EXAMPLE 1

- 23.4% by weight of dolomite Samin,
- 13.8% by weight of magnesia Nedmag, and
- 63.42% by weight of alumina Pechiney

are used at start (by dry weight of the binder) and the blend is burnt during 5 hrs at 1450°C. The composition of the final product is determined by X-ray fluorescence (Table I).

TABLE I
Composition of the resulting clinker

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
Percentage	0.1	71.4	0.2	8.6	19.6

The study of the resulting clinker by X-ray diffraction shows that only the desired phases are present, namely CA, CA₂ and MA (with C=CaO, A=Al₂O₃ and M=MgO).

The importance of the selection of the raw materials is obvious from the following comparative trials.

A second clinker is made according to the same operating mode as the former, but with different raw materials : the alumina is substituted for by gibbsite (hydrated alumina) by using the following proportions :

- 17.2% by weight of dolomite Samin,
- 10.1% by weight of magnesia Nedmag, and
- 72.7% by weight of gibbsite,

and the blend is burnt during 5 hrs between 1400°C and 1600°C.

For both clinkers, the combination ratio of the phases is measured by the ratio of the surfaces of X-ray diffraction peaks for MgO and MA spinel.

The results are shown in Table II.

TABLE II
Comparison of MgO/MA ratios
(ratio of surfaces of X-ray diffraction peaks)

Raw materials	MgO/MA
Dolomite/alumina/magnesia	0.06
Dolomite/gibbsite/magnesia	0.35

Thus, it has been shown that the combination ratio of magnesia with alumina to form the spinel depends upon the raw materials being used. The selection of these ones is thus quite fundamental.

The spinel obtained in the binder of example 1 with the blend of dolomite/alumina/magnesia has quite fine grains compared to commercially available spinels on the market. That is illustrated by a comparison of particle diameters between the spinel in the above-mentioned binder and the spinel sold under the trade name ALCOA AR78 DIN70.

Such a comparison is carried out through a measurement device sold under the trade name Malvern Mastersizer (model S) by calling on MIE theory with "3QHD" presentation, the particularities of which are a particle refraction index of 1.729, a particle absorption index of 0.1 and a refraction index of 1.33 for the bearing liquid. Thus, three lines from 23 to 25 (Fig. 3) are drawn, giving respectively for known spinels (lines 23 and 24) and the spinel of the binder above (line 25), depending on the particle diameter expressed in μm (axis 21), the cumulated percentage of the total volume (axis 22). Consequently, it has

been discovered that the spinel in the binder above comprises substantially smaller particles than those of known spinels.

EXAMPLE 2

A CMA clinker according to the invention is prepared from 23% dolomite, 13.5% magnesia and 63.5% alumina and the blend is burnt during 5 hrs at 1450°C and a CMA clinker is obtained with the following composition :

- CaO : 8.4%
- MgO : 20.4
- Al₂O₃ : 71.2.

The X-ray diffraction diagram for the burnt clinker shows that only the three expected phases CA, CA₂ and MA are present.

A refractory concrete is made with such a clinker by mixing the following raw materials (Table III) :

TABLE III

Raw materials for producing concrete

Raw materials	Mass %
Coarse granulates of tabular alumina ALCOA T60(0-7 mm)	61
Granulates of spinel Haicheng Houyin Magnesite Products MAS 76 (< 1 mm)	11
Reactive alumina fines ALCOA CT 3000 SG	10
CMA clinker above	18
Dispersants (mixture of polacrylates – Darvan 7C – and citric acid)	0.1

These ingredients are mixed with 4.7% of water with respect to the concrete formulation.

Following properties of such a refractory concrete are measured :

- a strong gas evolution of the concrete is observed, which shows that the concrete is assuming its location correctly without capturing air bubbles, so reducing the refractory porosity and then improving its resistance to slag corrosion;
- concrete stiffening of the concrete takes place after 40 minutes.

Standard conventional mechanical tests and corrosion tests show that the concrete suits to good behaviour requirements for applications such as a wear lining in steel ladles.

It can be also observed that the resulting concrete has a microstructure having an intergranular matrix made of very fine grains, particularly when compared with a refractory concrete obtained by directly mixing aluminous cement and magnesian spinel (Fig. 4 and 5).

In the following examples, the indications are as follows :

- "CMA 72 binder", a cement containing 72% of MA, 17% of CA and 11% of CA₂ by dry weight of the binder (nominal composition) produced according to an industrial process, and
- "CMA 80 binder", a cement containing 80% of MA, 15% of CA and 5% of CA₂ by dry weight of the binder obtained experimentally.

Reference is also made to the aluminous cement known under the trade name Secar 71 for comparison.

The following annotations are used thereafter :

- Alu Tab : tabular alumina,
- Mesh : number of openings per inch on a sieve,
- Alu React CT 3000 SG : reactive alumina commercially available under trade name CT 3000 SG in ALCOA company,
- Alu React P 152 SB : reactive alumina commercially available under trade name P 152 SB in PECHINEY company,
- HMP : fluidizing agent made of sodium hexametaphosphate,
- Chinese spinel : spinel commercially available in Haicheng Houyin company,
- S 71 : aluminous cement commercially available under trade name Secar 71,
- DARVAN 7 S : fluidizing agent.

EXAMPLE 3

Concretes based on CMA 72 and CMA 80 binders the compositions of which are given in Table IV and a concrete based on S71 binder the composition of which is given in Table V have been studied.

TABLE IV
Composition of CMA-based concrete

Reference	Concrete composition	
	Content (%)	Quantity (g)
Alu Tab ¼ - 8 Mesh	33.0	660
Alu Tab 8 – 14 Mesh	16.0	320
Alu Tab 28 - 48 Mesh	6.0	120
Alu Tab < 48 Mesh	5.0	100
Spinel 0.5 – 1 mm	7.5	150
Spinel 0 – 0.5 mm	3.5	70
ALU React CT 3000 SG	11.0	220
CMA 72 or 80 binder	18.0	360
TOTAL	100.0	2000
WATER	5.3	106
Sodium hexametaphosphate HMP	0.080	1.60
Boric acid	0.010	0.20

TABLE V
Composition of S71-based concrete

Reference	Concrete composition	
	Content (%)	Quantity (g)
Alu Tab ¼ - 8 Mesh	33.0	660
Alu Tab 8 – 14 Mesh	16.0	320
Alu Tab 28 - 48 Mesh	6.0	120
Alu Tab < 48 Mesh	5.0	100
Spinel 0.5 – 1 mm	9.0	180
Spinel 0 – 0.5 mm	4.0	80
Spinel 0 – 0.09 mm	10.0	200
ALU React CT 3000 SG	11.0	220
S71 binder	6.0	120
TOTAL	100.0	2000
WATER	5.3	106
Sodium hexametaphosphate HMP	0.080	1.60
Boric acid	0.010	0.20

Rheology and workability mentioned in Table VI are obtained.

TABLE VI
Rheology and workability of concretes

Reference test	Water (%)	Pouring test				Working time
		Vibrating table (mm)		ASTM table (%)		
		0 mn	30 mn	0 mn	15 mn	mn
S71	5.30	240	130	80	30	45
CMA 72	5.30	230	180	65	40	45
CMA 80	5.30	225	210	90	60	35

Table ASTM indicates a shock table for standard trials according to standard ASTM C230.

It has been discovered that concrete fluidities, represented by spreading measurements at different periods, are similar or higher in the case of CMA 80. Moreover, workabilities represented by the working time are identical, except for measurement uncertainties.

With a constant water content, adjuvantation for CMA 72 suits to CMA 80. It is to be noticed that the spinel enrichment of CMA 80 goes with a very significant fluidity gain. With a constant fluidity, the water content may be reduced. However, the concrete presents then a fall of mechanical performances (see example 5).

Such results show that the CMA 72 or 80 based concretes allow for a working time approximately equivalent to the one provided by the Secar 71 based solution.

EXAMPLE 4

Rheology and workability tests are made on the concrete of example 3 with CMA 72. The following trials implement two adjuvantations called respectively adj1 and adj2 and shown in Table VII. The results obtained for rheology and workability are given in Table VIII.

TABLE VII
Adjuvantations for concrete of example 3
(with CMA 72)

Reference	Composition of adjuvantation			
	adj1		adj2	
	Content (%)	Quantity (g)	Content (%)	Quantity (g)
Water	5.3	106	5.3	106
Sodium hexametaphosphate HMP	0.080	1.600	0.080	1.600
Boric acid	0.010	0.200	0.015	0.300

TABLE VIII
Rheology and workability (adj1 and adj2)

Reference test	Water (%)	Pouring test				Working time
		Vibrating table (mm)		ASTM table (%)		
		0 mn	30 mn	0 mn	15 mn	mn
adj1	5.30	230	180	65	40	45
adj2	5.30	220	185	70	30	50

Thus, it has been shown that the HMP content brings about concrete deflocculation and fluidity. Moreover, the boric acid addition does not make the workability longer significantly. The adj1 adjuvantation give thus a good compromise.

EXAMPLE 5

In such example, the results on the thermo-mechanical properties of concretes of example 3 through comparative tests with the concrete having a reference composition (S71 binder, that does not contain magnesian spinel) are given.

The mechanical performances of the concretes in cold conditions and after burning are given in Tables IX and X, wherein F and C are respectively the bending and compression resistances.

TABLEAU IX
Mechanical resistances in cold condition
and after stoving

Reference test	Water (%)	Mechanical resistances (Mpa)					
		In cold condition				After stoving at 110°C	
		F6h	C6h	F24h	C24h	F	C
S 71	5.30	-	-	5.3	57.7	12.8	100.7
CMA 72	5.30	1.3	13.8	6.6	64.6	10.9	98.9
CMA 80	5.30	0.6	9.6	4.6	36.9	10.2	83.1

5

TABLE X
Mechanical resistances after a thermal treatment and cold breaking

Reference test	Eau (%)	Mechanical resistances after a thermal treatment and cold breaking (Mpa)					
		F800°	C800°	F1100°	F1100°	F1500°	F1500°
		C	C	C	C	C	C
S 71	5.30	9.8	87.3	13.1	77.6	47.3	> 168
CMA 72	5.30	10.	110.8	17.4	112.2	37.9	> 168
CMA 80	5.30	9.9	105.0	16.4	111.2	32.4	> 168

10 It has been discovered that after a thermal treatment at 800°C, the mechanical resistances developed by the CMA are higher than those given by the S 71. Moreover, concrete keramization takes place at a lower burning temperature with CMA binders than with S 71 cement.

EXAMPLE 6

15 In this example, concrete slag corrosion has been studied. To do so, crucibles 30 (Fig. 6 and 7) are made in moulds so that each crucible 30 has a cubic shape with a width of l, one top side 32 of which is recessed with a cavity 31 forming a cylinder of a diameter d and a depth p. Dimensions l, d and p are for example respectively 100, 50 and 50 mm.

20 Concrete quantity required for making a bloc is 2.5 kg. For each test, two moulds are cast simultaneously. 5 kg of concrete are introduced into the bowl of Rayneri-type mixer, and then mixing water. Mixing is made at small

speed. Mixing is then poured into the shaping moulds, then the recessing core is put in place. A vibration of the mixture is carried out during 1 minute so as to remove air bubbles. For setting, the samples are arranged in a humid cabinet during 24 hrs at 20°C. The cubes are then released, dried in a stove at 110°C during 24 hrs, and then burnt in a muffle furnace at 1500°C during 6 hrs so as to keramize them. As the surface condition of the cube walls is not perfectly smooth, a surface treatment is carried out in the recess bottom with a flat bottom auger. Such surface is a reference for measuring the corrosion effect.

The corrosion trial consists in putting the slag-containing crucibles 30 in a temperature-controlled furnace during 24 hrs. During this period, the slag corrodes the concrete of the crucibles 30.

Before treatment, the depth p of the cavity recess 31 is measured precisely on each crucible block through a metal rule. The cavity 31 is then filled with slag. The block is introduced into a muffle furnace, in an envelope in alumina filled itself with alumina powder to prevent the furnace deterioration in case where there would be a cracking of the crucible 30. As specified formerly, a thermal treatment is carried out at 1500°C or 1600°C, with the following profiles :

- profile 1 : temperature rise of 100°C/hr up to 1500°C, holding time of 24 hrs, and then free fall down to 20°C;
- profile 2 : temperature rise of 100°C/hr up to 1600°C, holding time of 24 hrs, and then free fall down to 20°C.

After a thermal treatment, the resulting crucibles 35 have a cavity 37 (Fig. 8). They are chopped into two parts passing through the cavity centre 37. Typically, two discrete zones 38 and 39 are distinguished in the part damaged by the trial :

- corrosion, i.e. the block part destroyed by the slag (zone 38), and
- impregnation, i.e. the penetration depth of the slag in the concrete (zone 39).

The corrosion is calculated by a depth difference cavity before and after thermal treatment (cavities 31 and 37). The impregnation is evaluated by measuring the slag penetration in various points of the crucible 30.

Concretes having the compositions indicated in the Table XI are submitted to such a test. The samples are called by names in three parts : the first one indicates the binder (S 71, CMA 72 or CMA 80) , the second one,

alumina (A for ALCOA : CT 3000 SG, and P for PECHINEY : P 152 SB) and the third one, spinel (R for reference, H for HARBISON and Ch for Chinese).

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TABLE XI

[illegible]

HMP 0.08 + boric acid 0.01

The corrosion and impregnation thicknesses of the crucibles are reported in the Table XII. Moreover, it can be seen on pictures the condition of the crucibles after corrosion trials for S 71-A-R (Fig. 9) et CMA 72-A-R (Fig. 10) at 1500°C and 24 hrs.

5 Besides such observations, it is to be noticed that for the trials at 1600°C, which create particularly severe conditions, certain crucibles have visibly lost rapidly their content (identified by a star in the Table XII). The damaged thicknesses are thus smaller. However, at such a temperature, all the crucibles have finally been cracked and lost part of their content,
10 except the crucible CMA 80-A-R. The cracks have appeared in the locations where the wall thickness is the smallest. At 1500°C/24 hrs, the degradation of the crucibles is much more significant. The crucibles are not cracked and hold their content.

TABLE XII
Corrosion tests (24 hrs) at 1500°C or 1600°C

	1500°C		1600°C		
	Corrosion	Impregnation	Corrosion	Impregnation	Observations
S71-A-R	3 mm	2 mm	5 mm	5 mm	Cracked*
CMA	3 mm	0 mm	8 mm	10 mm	Very cracked
72-A-R	4 mm	1 mm	-	-	
CMA	6 mm	1 mm			
72-A-H					
CMA	5 mm	1 mm			
72-A-Ch					
CMA	5 mm	1 mm	5 mm	15 mm	Very cracked
72-P-R					
CMA	5 mm	0 mm	8 mm	5 mm	Very cracked
72-P-Ch					
CMA			4 mm	8 mm	Very cracked
72-P-H					
CMA			6 mm	2 mm	Not cracked
80-A-R					
CMA			4 mm	5 mm	Cracked*
80-P-Ch					
CMA			7 mm	6 mm	Cracked*
80-P-H					

- Rapid cracking → Flowing of slag out of the crucible and a small interaction.

At 1500°C, the formulations present all a small degradation, although the thicknesses are slightly weaker for the CMA-containing formula CMA 72-A-R. The substitution of the control spinel and/or the reactive alumina CT 3000 SG by other products does not modify the corrosion resistance properties. At 1600°C, these observations stay valid at the observable level.

Such results show the formulation flexibility for CMA compared to the raw materials. Such modifications do not create significant

CLAIMS

1. Clinker-type hydraulic binder obtained through burning comprising :

- 5 - a magnesian spinel mineralogical phase, and
 - at least a calcium aluminate mineralogical phase with a lime content of less than 15% of the binder by dry weight,
 characterized in that the magnesian spinel comprises between 68% and 81% of the binder by dry weight.

10 2. Binder according to claim 1, characterized in that the calcium aluminates are essentially made of CA and CA₂, with C=CaO and A=Al₂O₃.

 3. Binder according to claim 2, characterized in that the calcium aluminates CA and CA₂ comprise between 19% and 32% of the binder by
 15 dry weight.

 4. Binder according to claim 3, characterized in that it comprises by dry weight of the binder, $71 \pm 2\%$ of magnesian spinel, $18 \pm 2\%$ CA and $11 \pm 2\%$ CA₂.

 5. Binder according to any one of claims 1 to 4, characterized in
 20 that it is quasi-free from free residual MgO, at least as it can be observed on X-ray diffraction spectrum for the binder.

 6. Binder according to any one of claims 1 to 5, characterized in that it has the following chemical composition by dry weight of the binder :

- 25 - lime CaO : 4 to 12%
 - magnesia MgO : 19 to 23%
 - alumina Al₂O₃ : 69 to 74%.

 7. Binder according to claim 6, characterized in that it has the following chemical composition by dry weight of the binder :

- 30 - lime CaO : 8.4%
 - magnesia MgO : 20.4%
 - alumina Al₂O₃ : 71.2%.

 8. Binder according to any one of claims 1 to 7, characterized in that it comprises a SiO₂ content of less than 0.5% of the binder by dry weight.

9. Binder according to any one of claims 1 to 8, characterized in that it has a Blaine area surface at least equal to 3000 cm²/g.

10. Use of a binder according to any one of claims 1 to 9 for producing a refractory concrete.

5 11. Use of a binder according to claim 10, characterized in that the binder is complemented by magnesian spinel, preferentially of large size, so that the concrete contains between 20% and 30% of magnesian spinel by dry weight of the concrete.

10 12. Use of a binder according to claim 11, characterized in that the concrete is produced by mixing by dry weight of the binder :

- between 16 and 27% of the binder,
- between 2 and 13% of fine reactive alumina,
- between 0 and 19% of large spinel, and
- between 52 and 71% of alumina granulates,

15 and preferably :

- 18% of the binder,
- 11% of reactive fine alumina,
- 11% of large spinel, and
- 60% of alumina granulates.

20 13. Use of a binder according to any one of claims 10 to 12, characterized in that it is used in the manufacture of steel ladles (1), preferably for wear linings (5) of such steel ladles (1).

25 14. Process for producing a binder according to any one of claims 1 to 9, characterized in that the binder is made through frittering by burning of a blend of raw materials comprising dolomite, alumina and magnesia.

15. Process according to claim 14, characterized in that dolomite is natural.

30 16. Process according to any one of claims 14 or 15, characterized in that alumina is metallurgical.

17. Process according to any one of claims 14 to 16, characterized in that magnesia is reactive, preferably caustic, and has advantageously a grain size 100% lower than 100 µm, preferably lower than 40 µm.

19. Process according to any one of claims 14 to 18, characterized
5 in that burning is carried out at a temperature comprised between 1400°C
and 1600°C.

20. Process according to any one of claims 14 to 19, characterized in that the degree of progression of the burning is evaluated by measuring the free magnesia content by dry weight of the mixture.

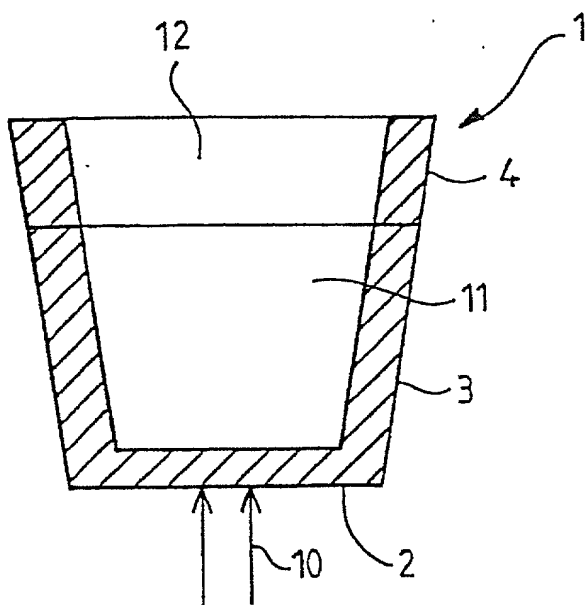


FIG. 1

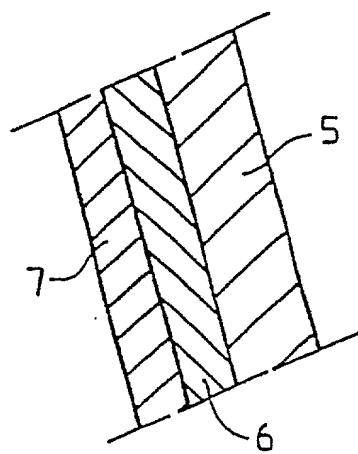


FIG. 2

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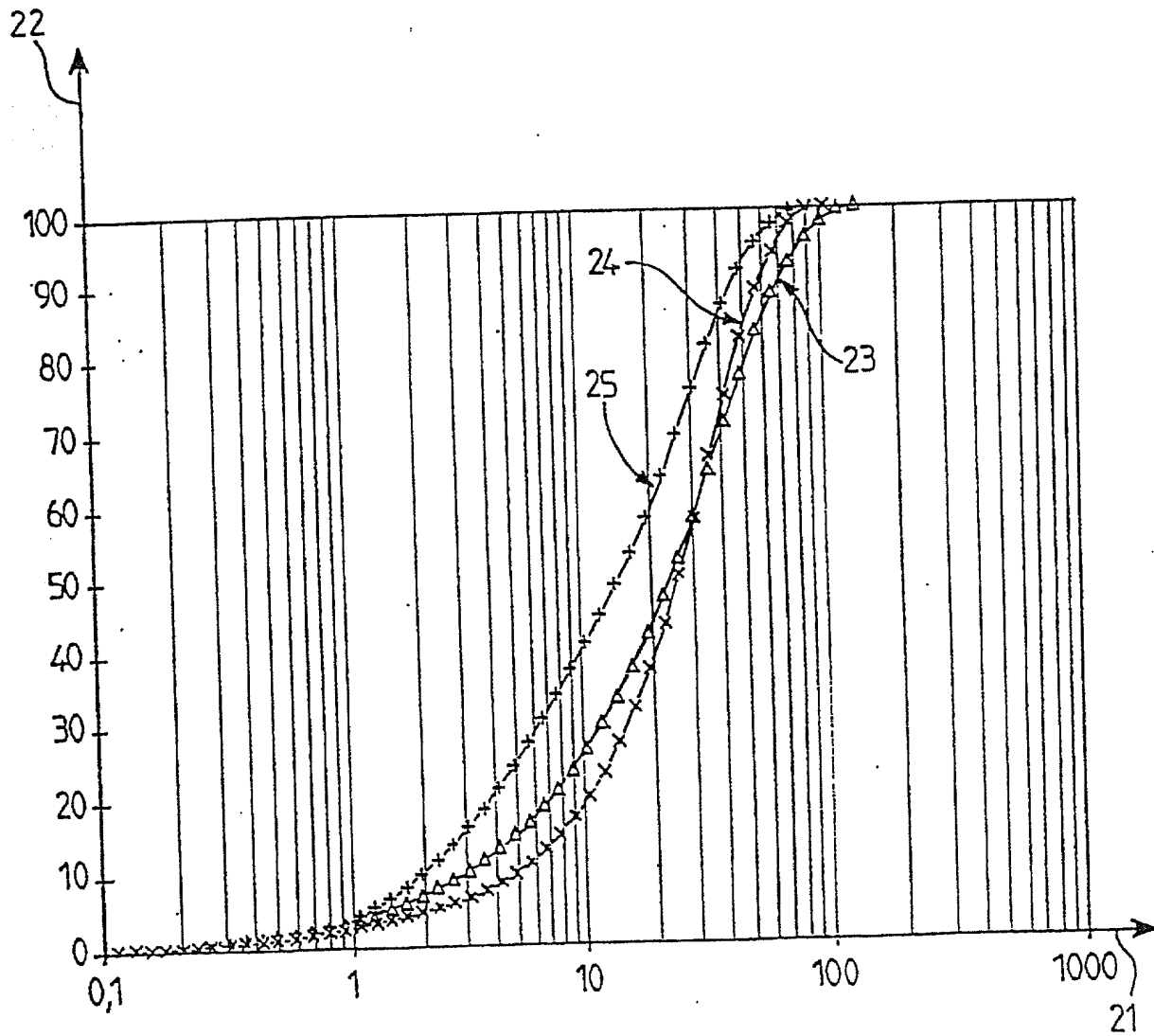


FIG. 3

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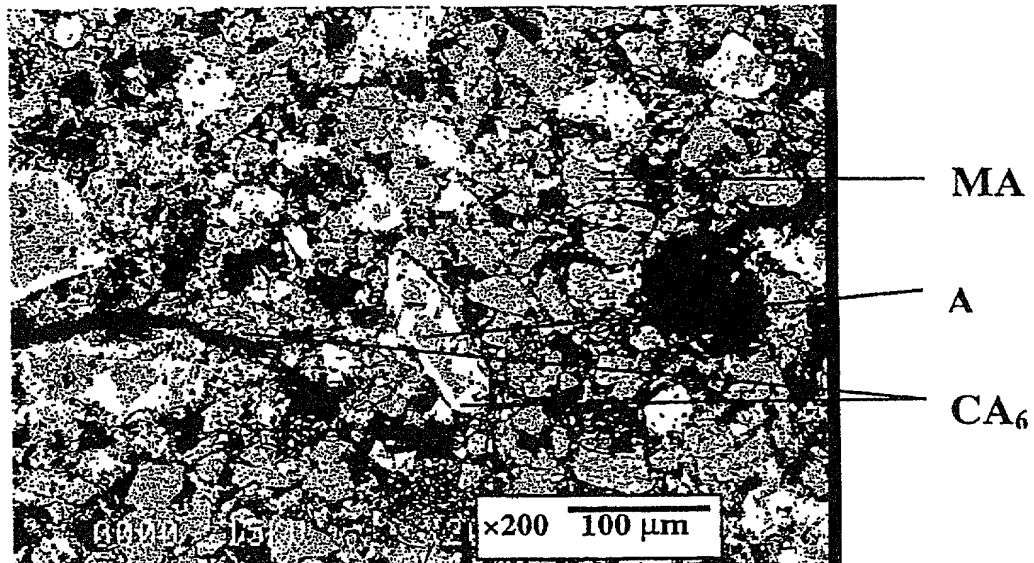


FIG. 4

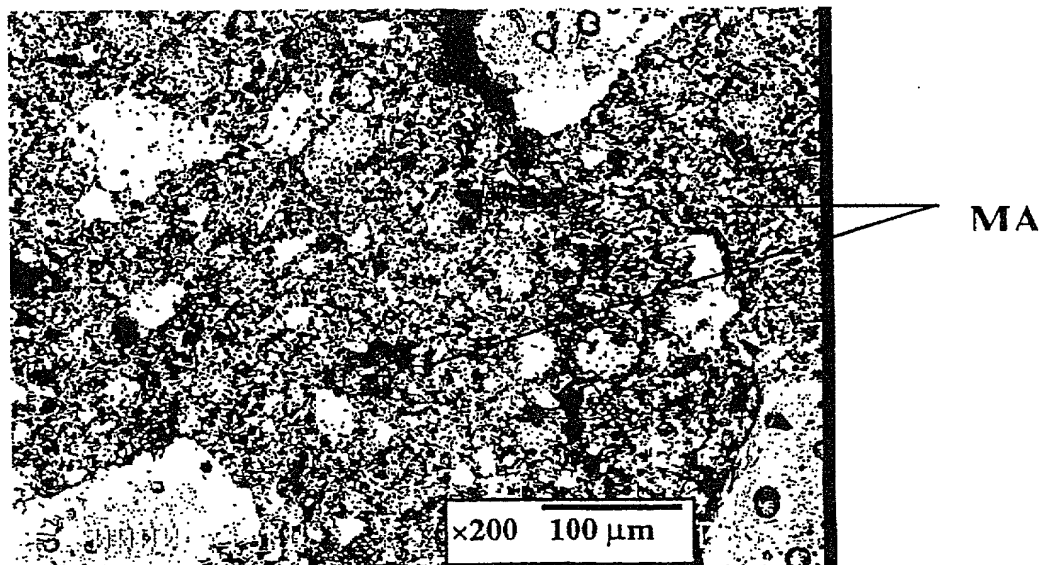


FIG. 5

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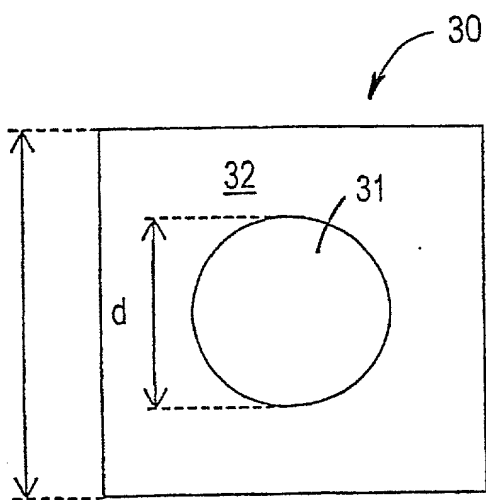


FIG. 6

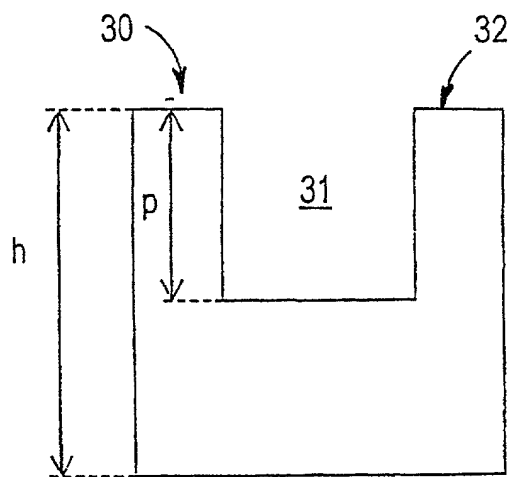


FIG. 7

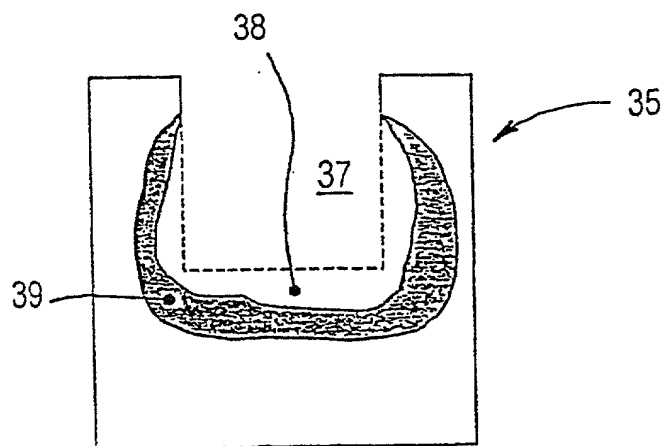


FIG. 8

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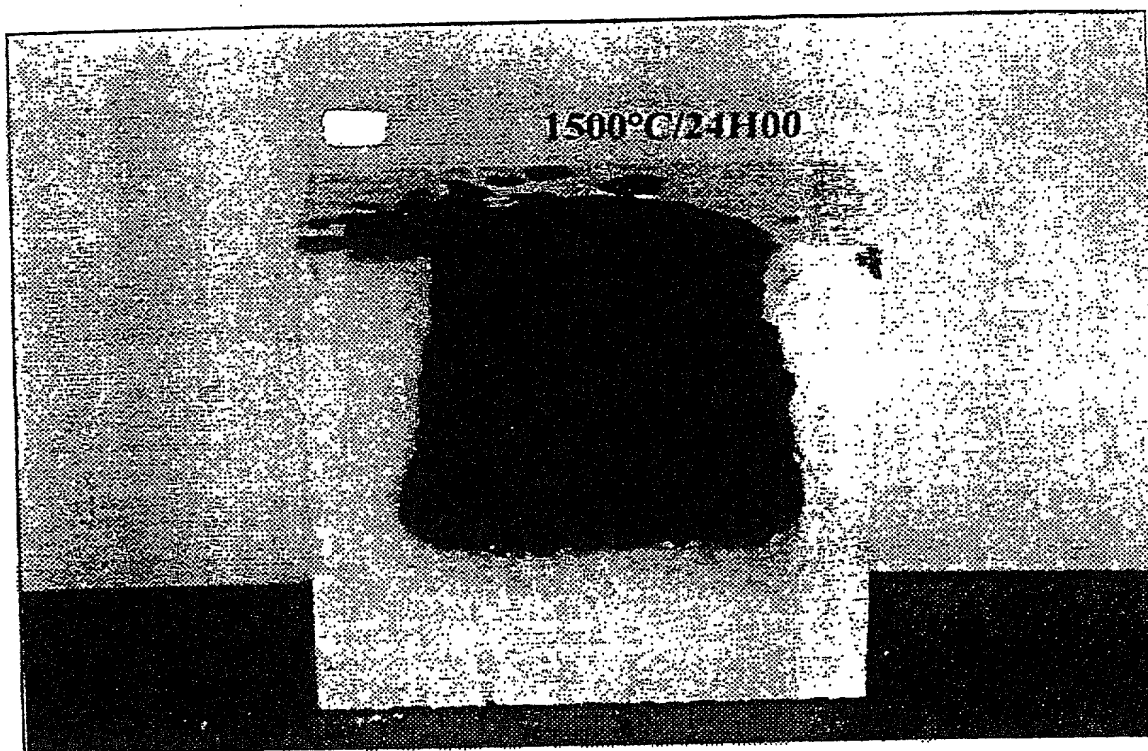


FIG. 9

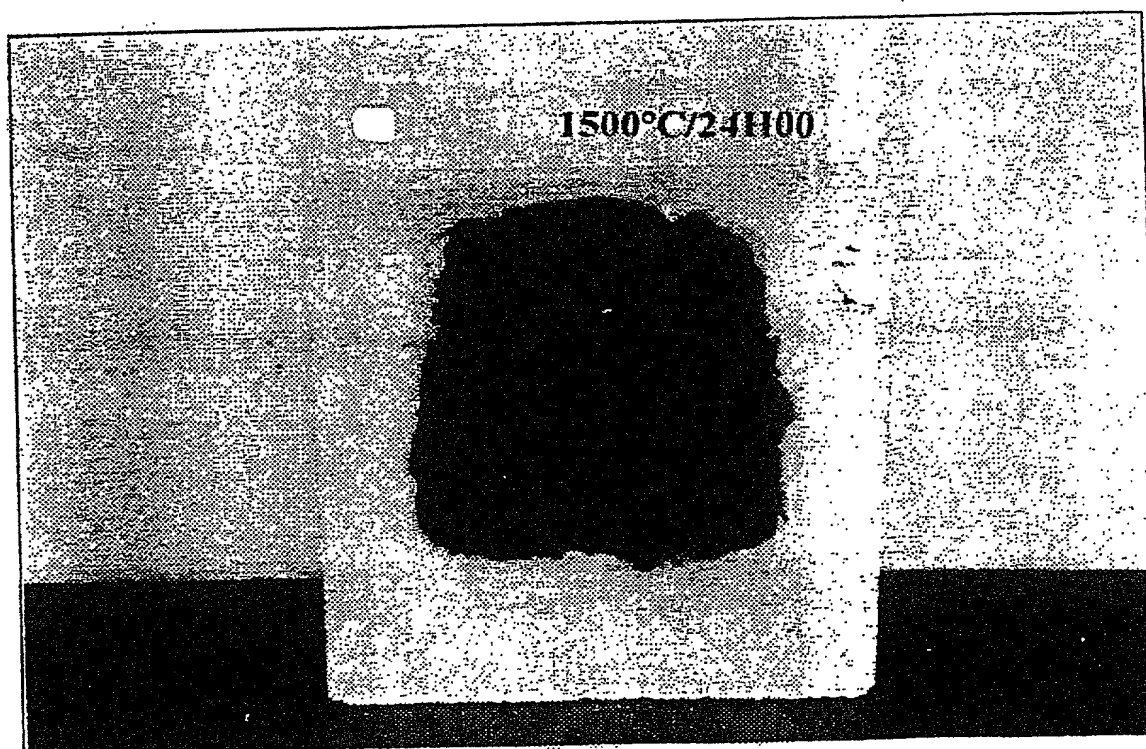


FIG. 10

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: Clinker hydraulic binder, use and method
for making same.

the specification of which: *(check one)*

REGULAR OR DESIGN APPLICATION

☐ is attached hereto.

☐ was filed on _____ as application Serial No. _____
(if applicable).

PCT FILED APPLICATION ENTERING NATIONAL STAGE

☒ was described and claimed in International application No. PCT/FR00/00167 filed on the 25th January 2000
and as amended on _____ (if any).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

PRIORITY CLAIM

I hereby claim foreign priority benefits under 35 USC 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN APPLICATION(S)

Country	Application Number	Date of Filing (day, month, year)	Priority Claimed
FRANCE	99 00842	26th January '99	YES

(Complete this part only if this is a continuing application.)

I hereby claim the benefit under 35 USC 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of 35 USC 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status—patented, pending, abandoned)

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The undersigned hereby authorizes the U.S. attorney or agent named herein to accept and follow instructions from _____ as to any action to be taken in the Patent and Trademark Office regarding this application without direct communication between the U.S. attorney or agent and the undersigned. In the event of a change in the persons from whom instructions may be taken, the U.S. attorney or agent named herein will be so notified by the undersigned.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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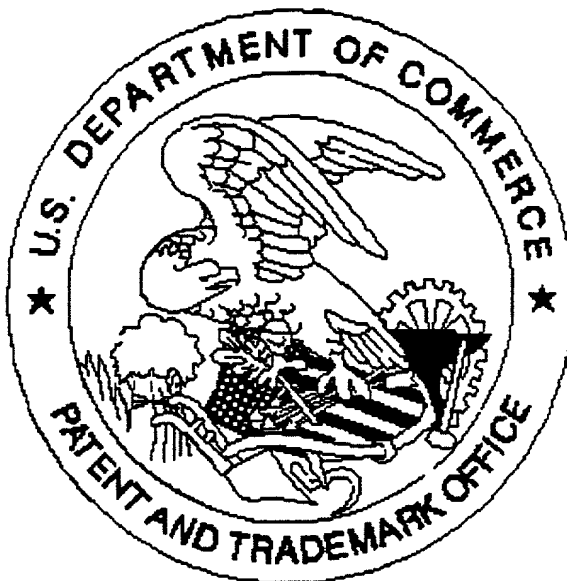
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